PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-309265

(43)Date of publication of application : 02.12.1997

(51)Int.Cl. B41M 5/00
B42D 15/00
C01B 33/20
D21H 19/38

(21)Application number : 08-171690

(22)Date of filing : 21.05.1996

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(54) INK JET RECORDING FILLER AND RECORDING PAPER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet recording filler wherein resistance to discoloration of an ink image, resistance to yellowing of paper, and its smoothness are excellent, and application in high density can be performed.

SOLUTION: An ink jet recording filler is composed of a porous globular silicate particle wherein that is composed of silicate of a composition of SiO2: MO=99.5:0.5 to 70:30 expressed by wt. ratio in oxide standard (in the formula, M represents periodic group D metals), the silicate is an X-ray diffractively amorphous or fine lamellar crystal, each particle is an independent distinct globular particle, a sphericity expressed by a ratio (DS/DI) of minor axis (DS) to major axis (DI) is within a ranqe of 0.8 to 1.0, and a particle size measured with an electron microscope is within a range of 0.3 to 20μm.

LEGAL STATUS

[Date of request for examination]	14.05.2003
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3802950

[Date of registration]	12.05.2006
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

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CLAIMS

[Claim(s)]
[Claim 1] the weight ratio of oxide criteria -- expressing -- SiO2 : It consists of the silicate of MO=99.5:0.5 thru/or a presentation (the inside M of a formula -- the [periodic table] -- II group metal is expressed) of 70:30. Said silicate It is an amorphous substance thru/or a detailed lamellar crystal in X diffraction study, and is the clear spherical particle which each particle became independent of. The sphericity expressed with the ratio (DS/DL) of the major axis (DL) of this particle and a minor axis (DS) is in the range of 0.8 thru/or 1.0. And the filler for ink jet record characterized by consisting of the porosity spherical silicate particle in the range whose particle size measured with the electron microscope is 0.3 thru/or 20 micrometers.
[Claim 2] The filler for ink jet record according to claim 1 which consists of the porosity spherical silicate particle whose specific surface area by the BET adsorption method is 50 thru/or 450m2 / g, whose pore volume is 0.5 thru/or 1.5 ml/g and, whose average pore radii are 20 thru/or 60A.
[Claim 3] The filler for ink jet record according to claim 1 or 2 with which a porosity spherical silicate particle has the oil absorption of 150 or more ml/g.
[Claim 4] The filler for ink jet record given in claim 1 thru/or any of 3 they are. [in which a porosity spherical silicate particle has the refractive index of 1.45 thru/or 1.56]
[Claim 5] A porosity spherical silicate particle is the acid-strength function H0. Filler for ink jet record given in claim 1 thru/or any of 4 they are. [which has the acidity 0.1 millimols / more than g in the range to +3.3 exceeding -3.0]
[Claim 6] A porosity spherical silicate particle is a filler for ink jet record given in claim 1 thru/or any of 5 they are. [which is what has the water dispersion pH of 6 thru/or 11]
[Claim 7] the amorphous silica spherical particle from which the porosity spherical silicate particle was obtained with the condensation grown method -- the [periodic table] -- the filler for ink jet record given in claim 1 thru/or any of 6 they are. [which is obtained by making the oxide, the hydroxide, or the water-soluble salt of II group metal act]
[Claim 8] The ink jet recording paper characterized by containing the filler for ink jet record given in any [claim 1 thru/or] of 7 they are.
[Claim 9] They are per [0.5] whole thru/or **** for ink jet record according to claim 8 contained 40% of the weight about the filler for ink jet record.
[Claim 10] **** for ink jet record according to claim 8 or 9 whose Beck smoothness it measures in the condition of having not carried out calender processing, and is 50 seconds or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] About the ink jet recording paper which used the filler for ink jet record, and this, more, this invention is excellent in the color fastness of an ink image, the xanthochroism-proof of paper, and smooth nature at a detail, and relates to the filler for ink jet record in which the coating in high concentration is possible.
[0002]
[Description of the Prior Art] ink jet record has little noise, high-speed record is possible for it, and, moreover, multiple-color-izing is easy for it -- etc. -- there is an advantage and application to various printers, facsimile, etc. is performed. As the recording paper used for this application, use at the point of the engine performance is difficult, and usual paper of fine quality and coat paper require properties, like that the ink droplet adhering to space is promptly absorbed in paper, that the flare of the ink droplet on space and a blot are controlled, that a clear image with concentration is formed, and this image is excellent in many robustness.
[0003] In order to give these properties to the front face of a paper substrate, various inorganic solid matter Applying to a paper front face with a binder as occasion demands, or inner-**(ing) is proposed. For example, the thing for which a synthetic silica and/or its salt are used (JP,57-157786,A), weak acid salts and oxides, such as a divalent metal, for example, magnesium, or zinc, -- an enveloping layer -- carrying out -- ****** -- things (JP,58-94491,A) -- Natural zeolite, permutite, the diatom earth, synthetic mica, etc. are made to contain in an enveloping layer (JP,59-68292,A), Using clay, talc, a calcium carbonate, a kaolin, the acid clay, the activated clay, etc. as white pigments which form an ink absorption layer (JP,58-89391,A and JP,59-95188,A) etc. is already known.
[0004] However, there is never no filler used for the ink jet recording paper at the thing that what is necessary is just to only absorb ink, and fixed balance is required between absorption of the whole ink, or adsorption of water or a solvent and adsorption of a color. For example, though the flare of an ink droplet and a blot are prevented when the absorption to the loading material layer of ink arises quickly, when a color etc. permeates into a loading material layer, the image formed tends to lack in concentration or clearness. It will be understood that it is not easy a thing to satisfy demand of preventing the flare of an ink droplet and a blot, and demand of raising the concentration and clearness of an image to coincidence in ink jet record in this way. Moreover, although the ink for ink jets generally consists of the constituent which dissolved the color in the medium which carries out the content of water and the little organic solvent The loading material currently used conventionally is not yet enough in the adsorption balance of each component in ink. For example, if the diameter of a dot becomes small, and a white spot omission arises in the ** TA section and the rate of adsorption of a color is too small when the rate of adsorption of a color is too large, the perfect circle nature of a dot will no longer be obtained.
[0005] As what improves these points, this invention person etc. sets to JP,4-60434,B and JP,4-60435,B previously. It measures by the Coulter counter method, measures by 2 thru/or the median size of 15 micrometers, the oil absorption of 180ml / 100g or more, and the solvent method, and is 1.450. It has the above refractive index. the [the amorphous silica which has the amount of moisture absorption in the conditions made to absorb moisture at the relative humidity of 90%, and the temperature of 25 degrees C for 200 hours in 35% or more of within the limits, and / of this amorphous silica / periodic-table] -- it proposed using the coated particle of II group metallic compounds as a loading material for the ink jet recording papers.
[0006] Moreover, using a spherical silica is indicated by JP,62-183382,A and JP,63-13776,A as a filler for ink jet record.
[0007]
[Problem(s) to be Solved by the Invention] Although the filler given in a public notice official report mentioned

above was excellent to be sure in respect of the adsorption balance of ink, it had the inclination which the strike-through of ink produces, and was not what may still be satisfied enough in respect of the clearness of an image, or the commodity value of printed matter. Furthermore, they are an indeterminate form, and amorphous silica given [this] in an official report and its coated particle have the quite high viscosity of coating liquid, therefore must make filler concentration in coating liquid quite low, must perform spreading on paper, and its workability of coating is bad and they have a fault, like the heat energy cost for desiccation becomes high.

[0008] On the other hand, although the filler for ink jet record which consists of a spherical silica has the advantage that filler concentration in coating liquid can be made high, it also has the fault of the color fastness of an ink image being still inadequate, and being easy to yellow paper during preservation.

[0009] this invention persons -- the [periodic table] -- containing II group metal component by the specific quantitative ratio, in X diffraction study, it excels in the color fastness of an ink image, the xanthochroism-proof of paper, and smooth nature, and moreover, the coating in high concentration is possible for the porosity spherical silicate particle of an amorphous substance thru/or a detailed lamellar crystal, and it found out that it could become the outstanding filler for ink jet record.

[0010] That is, the purpose of this invention is excellent in the color fastness of an ink image, the xanthochroism-proof of paper, and smooth nature, and is to offer the filler for ink jet record in which the coating in high concentration is possible.

[0011]

[Means for Solving the Problem] according to this invention -- the weight ratio of oxide criteria -- expressing -- SiO2 : It consists of the silicate of MO=99.5:0.5 thru/or a presentation (the inside M of a formula -- the [periodic table] -- II group metal is expressed) of 70:30. Said silicates are an amorphous substance thru/or a detailed lamellar crystal in X diffraction study, and it is the clear spherical particle which each particle became independent of. The sphericity expressed with the ratio (DS/DL) of the major axis (DL) of this particle and a minor axis (DS) is in the range of 0.8 thru/or 1.0 especially 0.9 thru/or 1.0. And the filler for ink jet record characterized by consisting of the porosity spherical silicate particle which has 20 micrometers of particle size measured with the electron microscope in 0.3 thru/or the range which is 3 thru/or especially 15 micrometers is offered.

[0012] According to this invention, the ink jet recording paper characterized by coming to contain the above-mentioned filler for ink jet record again is offered.

[0013] The filler for ink jet record used for this invention 1. The specific surface area by the BET adsorption method is 50 thru/or 450m2 / g especially 100 thru/or 400m2 / g. Pore volume 1.5 ml/g, it is especially 0.6 thru/or 1.3 ml/g, and an average pore radius consists [0.5 thru/or] of a 20 thru/or porosity [which is 30 thru/or especially 60A 60A] spherical silicate particle, 2. A porosity spherical silicate particle has especially 150 or more ml/g of oil absorption of 160 thru/or 250 ml/g, 3. A porosity spherical silicate particle has the refractive index of 1.45 thru/or 1.56, 4. A porosity spherical silicate particle is the acid-strength function H0. It has the acidity of 0.2 thru/or 0.7 millimols / g especially more than 0.1 millimols / g in the range to +3.3 exceeding -3.0, 5. Porosity spherical silicate particles are 6 thru/or 11, and the thing that has especially the water dispersion pH of 7 thru/or 10, 6. -- the amorphous silica spherical particle from which the porosity spherical silicate particle was obtained with the condensation grown method -- the [periodic table] -- obtaining-by making oxide, hydroxide, or water-soluble salt of II group metal act ** is desirable.

[0014] The ink jet detail paper of this invention measures the filler for 7. ink jet record 40% of the weight in per [0.5] whole thru/or containing especially in 3 thru/or 20% of the weight of an amount, and the condition of having not carried out 8. calender processing, and its being [the Beck smoothness / 50 thru/or especially 100 seconds]-50 seconds or more ** is desirable.

[0015]

[Embodiment of the Invention] the porosity spherical silicate particle used for this invention -- the weight ratio of (A) oxide criteria -- expressing -- SiO2 : having the presentation (the inside M of a formula -- the [periodic table] -- II group metal being expressed) of MO=99.5:0.5 thru/or 70:30 -- (B) It is [that they are an amorphous substance thru/or a detailed lamellar crystal in X diffraction study,] the clear spherical particle which the particle of (C) each became independent of, (D) It has the description about the combination of being in the range whose particle size measured with that the sphericity expressed with the ratio (DS/DL) of the major axis (DL) of a particle and a minor axis (DS) is in the range of 0.8 thru/or 1.0 and the (E) electron microscope is 0.3 thru/or 20 micrometers.

[0016] namely, this porosity spherical silicate particle -- the [periodic table] -- while being able to prevent yellowing of the recording paper by containing II group metal component by the weight ratio of the above (A), the ink formed can raise the color fastness of an image. the [namely, / the case where amorphous silica is used as shown in the

example mentioned later, and / periodic table] -- yellowing under preservation when the amount is lower than the above-mentioned range though II group metal component is contained, although an inclination is remarkable and there is an inclination discolored when an ink image is put to light or air the [periodic table] -- by combining II group metal component by the above-mentioned quantitative ratio, and considering as a salt, these defects are cancelable. on the other hand -- the [periodic table] -- if there are more amounts of II group metal component than the above-mentioned range, since the absorptivity over ink will fall, it is not desirable.

[0017] The above-mentioned particle used for this invention is porosity, and, moreover, it is the descriptions as the above-mentioned requirements (B) that they are an amorphous substance thru/or a detailed lamellar crystal in X diffraction study. Although a detailed lamellar crystal shows the X diffraction image similar to phyllosilicate, it means what has a weak diffraction peak (1/4 or less [Generally]) compared with usual phyllosilicate.

[0018] Drawing 1 of an accompanying drawing shows the X diffraction image of an amorphous porosity spherical silicate particle used for this invention, drawing 2 shows the X diffraction image of the porosity spherical silicate particle of a detailed lamellar crystal, and drawing 3 shows the X diffraction image of an amorphous porosity spherical silicic-acid particle used as a manufacture raw material of these silicates.

[0019] By taking the structure of an amorphous substance thru/or a detailed lamellar crystal by porosity, this spherical silicate particle shows adsorbent [which were excellent to ink / the absorptivity and adsorbent], and gives the image which moreover does not have a blot at high concentration.

[0020] Furthermore, as the above-mentioned requirements (C) and (D), the porosity spherical silicate particle used for this invention is a clear spherical particle which each particle became independent of, and it is important for it that sphericity (DS/DL) is 0.9 especially or more 0.8 or more. Condensation does not have a primary particle as it is the clear spherical particle which each particle became independent of, and mutually-independent is carried out and it means that the primary particle is moreover making the shape of a clear ball.

[0021] Drawing 4 of an accompanying drawing is an electron microscope photograph in which the particulate structure of the amorphous porosity spherical silicate particle (thing of the X diffraction image of drawing 1) used for this invention is shown, drawing 5 is an electron microscope photograph in which the particulate structure of the porosity spherical silicate particle (thing of the X diffraction image of drawing 2) of a detailed lamellar crystal is shown, and drawing 6 is an electron microscope photograph in which the particulate structure of the amorphous porosity spherical silicic-acid particle (thing of the X diffraction image of drawing 3) used as a manufacture raw material of these silicates is shown.

[0022] Since the porosity spherical silicate particle of this invention has the above-mentioned particulate structure, it can form high-concentration dispersion liquid, moreover the porosity spherical silicate particle forms a closest packing condition or the restoration condition near this in a paper front face, and there is no strike-through of ink at the time of image formation, and it gives the advantage that a clear image can moreover be formed while it is excellent in the dispersibility to the inside of coating liquid.

[0023] Moreover, this porosity spherical silicate particle should have the particle size measured with the electron microscope in the range which is 0.3 thru/or 20 micrometers. When particle size is lower than the above-mentioned range, since the yield of a filler worsens on the occasion of manufacture of the recording paper and the condensation inclination of a primary particle also increases, it is not desirable. If particle size becomes larger than the above-mentioned range, since the smooth nature of the recording paper will be lost on the other hand, it is not desirable too.

[0024] The filler for ink jet record used for "filler for ink jet record" this invention has the following characteristic additional physical properties according to the above-mentioned description.

[0025] namely, that this porosity spherical silicate particle is porosity and a specific surface area according to a BET adsorption method in relation to amorphous thru/or being a stratified fine crystal -- 50 thru/or 450m2 / g -- especially -- 100 thru/or 400m2 / g -- it is -- pore volume -- 0.5 thru/or 1.5ml/g -- especially -- 0.6 thru/or 1.3 ml/g -- it is -- and an average pore radius -- 20 -- or 60A is 30 thru/or especially 60A. These properties are very important about the absorptivity of ink, prevention of an adsorbent blot, etc.

[0026] Moreover, although it relates also to the above-mentioned property, as for especially a porosity spherical silicate particle, it is desirable to have the oil absorption of 160 thru/or 250 ml/g 150 or more ml/g.

[0027] Furthermore, as for a porosity spherical silicate particle, it is desirable to have the refractive index of 1.45 thru/or 1.56 in respect of the clearness of an image.

[0028] Furthermore, as for especially a porosity spherical silicate particle, it is desirable that the acid-strength function H0 has the acidity of 0.2 thru/or 0.7 millimols / g more than 0.1 millimols / g in the range to +3.3 exceeding -3.0 in respect of the robustness of an image again.

[0029] Moreover, although a porosity spherical silicate particle is related also to said chemical composition, it is

advantageous that they are 6 thru/or 11, and the thing that has especially the water dispersion pH of 7 thru/or 10 in respect of chemical stability.

[0030] the amorphous silica spherical particle from which the porosity spherical silicate particle was obtained with the condensation grown method be [easy although / it] it was manufactured by the manufacturing method of arbitration when the porosity spherical silicate particle used for this invention had the above-mentioned description -- the [periodic table] -- it is desirable the oxide of II group metal, a hydroxide, or to be obtained by carrying out a water-soluble salt operation. The amorphous silica spherical particle by the detailed corning method can also be used as a raw material. Although this example is explained below, this invention is never limited to this.

[0031] (1) The amorphous silica system spherical particle of the porosity used as a condensation grown method silica raw material is obtained also by neutralizing from an acid, after mixing a silicic-acid alkali water solution, a water-soluble polymer, and the acid water solution of the amount of partial neutralization, making the granular object which leaves this mixed liquor and consists of the partial neutralization object of silicic-acid alkali generate and separating this granular object.

[0032] As silicic-acid alkali used as a raw material, m is the number of the number of 1 thru/or 4 especially 2.5 thru/or 3.5 among following type,Na2.O.mSiO2.type. The silicic-acid alkali which has,******, especially the water solution of a sodium silicate are used. The presentation of this silicic-acid alkali is related to the stability of mixed liquor, the yield of the granular object to generate, and grain size.

[0033] the concentration of silicic-acid alkali -- SiO2 in the inside of mixed liquor ****** -- it is good to make it concentration serve as 3 thru/or range which is 4 thru/or especially 8 % of the weight 10% of the weight.

[0034] In this condensation grown method, a water soluble polymer is used as a condensation growth agent of a particle silica. As a condensation growth agent, although a carboxymethyl cellulose (CMC) is the most suitable, an acrylamide system polymer and other water soluble polymers can be used for others. A condensation growth agent is per all silicas in a silicic-acid alkali solution, and SiO2. It is used 100% by weight criteria in 1 thru/or the amount used as 5 thru/or especially 50 % of the weight.

[0035] By this approach, the condensation growth assistant which consists of a water-soluble inorganic electrolyte or other water soluble polymers can also be used in CMC and combination. As a water-soluble inorganic electrolyte, it is water solubility, and although the thing of arbitration can be used if it is the inorganic electrolyte which has agglutination to a sol etc., the mineral-acid salt or organic-acid salt of the 1st group of the periodic table, the 2nd group, the 3rd group, the 4th group metal, or other transition metals is used, and the suitable example is as follows.

[0036] an alkali-metal salt, for example, NaCl, and Na2 SO4 etc. -- mineral-acid salt [of alkali metal]; -- other water-soluble metal salts, such as mineral-acid salt; zinc chlorides, such as an alkaline-earth-metal salt, for example, a calcium chloride, a magnesium chloride, magnesium sulfate, and a calcium nitrate, a zinc sulfate, an aluminum sulfate, an aluminum chloride, and sulfuric-acid titanyl.

[0037] Moreover, other water soluble polymers can also be used as a condensation growth agent or a condensation growth assistant, and compatibility with CMC can also use the macromolecule of the Nonion systems, such as good starch and guar gum, locust bean gum, gum arabic, tragacanth gum, PURITE issue gum, crystal gum, SENEGARUGAMU, PVA, a MECHIRU cellulose, sodium polyacrylate, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, and a polyethylene glycol, for this purpose.

[0038] As an acid used for neutralization, although various inorganic acids and organic acids are used, it is good to use mineral acids, such as a sulfuric acid, a hydrochloric acid, a nitric acid, and a phosphoric acid, and the sulfuric acid is most excellent from the economical standpoint, also among these in respect of the yield of a granular object, and the uniformity of particle size and a gestalt. In order to perform a homogeneous reaction, it is good although using in the form of a dilution water solution uses it by 1 thru/or 15% of the weight of concentration often and generally. Furthermore, water-soluble electrolytes, such as NaCl, especially acid salt, and neutral salt may be added to these acids. The amount of the acid used even if it faces mixing is good for pH of mixed liquor to use in 10.2 thru/or 11.2, and an amount that is set especially to 10.5 thru/or 11.0 so that partial neutralization may generate a homogeneous mixed solution (it is transparent).

[0039] By this approach, an acid may be added, after adding a condensation growth agent after there being no limit in the addition sequence of each above-mentioned component, for example, adding an acid to a silicic-acid alkali water solution, and adding a condensation growth agent to a silicic-acid alkali water solution conversely. Naturally these may be added to coincidence. When using a condensation growth assistant, this condensation growth assistant may be used as an aquosity medium for adding each component, or may be beforehand added in an acid. Each component is mixed enough, after making it homogenize, this mixed liquor is put and the granular object of a partial neutralization object is deposited.

[0040] as this deposit condition -- general -- 0 thru/or 100 degrees C -- suitable -- the temperature of 10 thru/or 40 degrees C -- 1 -- or 3 thru/or neglect of about 20 hours are suitably suitable for 50 hours. The particle size of a deposit particle becomes large, so that temperature is generally low, and the particle size of a deposit particle becomes small, so that temperature is high. The particle size of a granular object can be controlled by control of temperature in this way. After the particle which separated the depositing particle and the depositing mother liquor and was re-distributed in water adds an acid and neutralizes, let it be the raw material for processing which operated rinsing, desiccation, a classification, etc. and was mentioned above. Since non-deposited a part for a silica and a condensation growth agent contain in the separated mother liquor or the dispersion liquid after neutralization, these can be reused effective in the following mixed deposit.

[0041] Moreover, it is per [SiO / 2] all silica weight if needed, using the silica sol, the silica gel, or the anhydrous silica powder of arbitration with a detailed particle size as a nucleating additive or an extending agent at mixed liquor. It can also add beforehand in the amount mentioned above on criteria. As for the silica to be used, it is desirable to have a submicron particle size.

[0042] (2) The method of corning silica gel particle dispersion liquid and a porous amorphous silica system spherical particle are faced making the sol which mixes a silicic-acid alkali solution and a mineral acid in an instant, is made to form a sol, and is formed emit into a gas medium, and making gel form, and are manufactured also by making either [at least] a silicic-acid alkali solution or a mineral acid distribute a water-insoluble nature solid particulate as a macro pore improver.

[0043] The silicic-acid alkali which has the presentation mentioned above as silicic-acid alkali, especially the water solution of a sodium silicate are used.

[0044] The concentration of silicic-acid alkali is SiO2. The concentration of 100 thru/or 225g/l and the thing which has especially the concentration of 130 thru/or 150g/l are suitable on criteria.

[0045] As an acid, although various inorganic acids and organic acids are used, it is good to use mineral acids, such as a sulfuric acid, a hydrochloric acid, a nitric acid, and phosphoric acid, and the sulfuric acid is most excellent from the economical standpoint, also among these in respect of the uniformity of the engine performance of spherical silica gel, particle size, and a gestalt. In order to perform a homogeneous reaction, it is good for using in the form of a dilution water solution to use it by 1 thru/or 15% of the weight of concentration often and generally.

[0046] Although concordance (compatibility) is in an aquosity medium by water-insoluble nature, and an inorganic thing can also use an organic thing widely as a solid particulate added in silicic-acid alkali or an acid if stable, generally an inorganic thing is desirable.

[0047] as an inorganic solid particulate -- the [periodic table] -- the [an III A group and] -- the [an IVA group and] -- the [an IVB group and] -- the [VB group or] -- VIII The oxide, the multiple oxide, hydroxide, or compound hydroxide of a group element can be mentioned. Specifically, an alumina, a silica, a titania, a zirconia, a vanadium oxide, niobium oxide, chromic oxide, molybdenum oxide, tungstic oxide, ferrous oxide, cobalt oxide, nickel oxide, oxidization palladium, oxidization platinum, zirconium silicate, etc. are mentioned.

[0048] Also among these, a silica, an alumina, a titania, or a zirconia is suitable, especially as amorphous silica and an alumina, as a silica, specific surface area, such as a gibbsite mold aluminum hydroxide and pseudo-boehmite mold alumina gel, is used, and the thing 50m2 / more than g is used advantageously.

[0049] Moreover, as an inorganic solid particulate, the clay or the zeolite of a TEKUTO aluminosilicate or a FIRO aluminosilicate especially nature, or composition can be used. As a clay mineral, a montmorillonite, beidellite, nontronite, saponite, hectorite, a sauconite, halloysite, pyrophyllite, a kaolinite, antigorite, sepiolite, a palygorskite, a vermiculite, etc. can be mentioned. As a zeolite, the various zeolites of A mold, an X type, Y mold, and P type, mordenite, Silicalite, and ZSM-5 grade can be mentioned. Moreover, these acid-treatment objects and burned products can also be used.

[0050] It is desirable that they are the mean particle diameter whose solid particulates are 0.1 thru/or 15 micrometers, and the particle which has the mean particle diameter which is 0.3-2 micrometers especially.

[0051] Even if it makes a silicic-acid alkali solution distribute a solid particulate, a mineral acid may be distributed, a solid particulate stable to alkali, for example, an aluminum hydroxide, is good to add to silicic-acid alkali, and a solid particulate stable in an acid on the other hand, for example, amorphous silica, is good to add to a mineral acid.

[0052] A solid particulate (SP) is the silica (SiO2) criteria in silicic-acid alkali, and is SiO2. : It is good to use in SP=95:5 thru/or 55:45, and the amount that serves as a weight ratio of 85:15 thru/or 70:30 especially.

[0053] The silicic-acid alkali solution or mineral acid which distributed the solid particulate should have the viscosity of 20 or less centipoises, and, moreover, can carry out extremely mixing with silicic-acid alkali and a mineral acid to homogeneity by maintaining to the above-mentioned viscosity in the inside of a short time.

[0054] Supply the silicic-acid alkali and the mineral acid which were manufactured in this way and by which the solid particulate was added by at least one side to a two fluid nozzle, mix both in an instant and a sol is made to form, and subsequently to the inside of a gas medium it emits, and is made to gel by this approach.
[0055] As for the supply ratio of the silicic-acid alkali and the mineral acid to a two fluid nozzle, it is good that it is that from which pH at the time of mixing is set to 6 thru/or 11, and although various ratios of a flow rate are changed and being dealt in them, it is desirable that it is generally in the range of 70:30 thru/or 50:50.
[0056] As a two fluid nozzle, it has the container liner section and the outer case section, and the nozzle which has a delivery in the point of the container liner section at the point of the mixed section and the mixed section is used, one fluid is supplied to the container liner section, and what has the path of the fluid of another side in the annular section between the container liner section and the outer case section is suitable. In order to supply a fluid to the container liner section and the annular section, when introducing a fluid into the tangential direction and producing a revolution style enables momentary mixing, it is desirable, and it is most desirable that both revolution direction is the reverse sense mutually. Although it generally is not required, the guide vane for revolution style generating can also be prepared as indicated by JP,48-13834,B.
[0057] The silica sol breathed out from a two fluid nozzle is gelled being maintained at the form of a drop in a gas medium, and serves as a spherical silica hydrogel. The regurgitation of the hydrosol from a nozzle may go in the direction of arbitration, may go to decline in the shape of a cone, and may be performed to facing up or sideways.
[0058] It is good for the fall direction of a silica hydrogel to form the receptacle tank of the silica hydrogel which held the aquosity medium. It is desirable to make aging or dealkalization of a silica hydrogel etc. perform in this receptacle tank.
[0059] If it invests in the dilute-alkali water solution to the receptacle tank, while being able to collect generally, without crushing a silica hydrogel, the silica gel the engine performance and whose configuration were stable can be obtained by riping this. 4 thru/or about 16 hours are suitable for aging processing at 40 thru/or the temperature of 15 degrees C.
[0060] The silica hydrogel which finished aging processing has that good of ** given to the dealkalization processing by acid treatment, in order to remove the alkalinity which remains in gel. This dealkalization processing uses pH1 thru/or the acid water solution of 3.5, and 8 thru/or processing of about 24 hours are appropriate for it at 40 thru/or the temperature of 15 degrees C.
[0061] The silica gel which finished these processings is ** given to washing processing. Washing processing is good to use a stream, and for pH to be in the range of 7.5**0.1, and to make it conductivity serve as the range of 50mS(s).
[0062] the obtained silica hydrogel -- as it is -- the [periodic table] -- it can use for a reaction with II group metal component, and this can be dried and it can also use for a reaction as xerogel of a silica.
[0063] (3) the [which is used for manufacture of the manufacture silicate of a silicate / periodic-table] -- as an II group metal component, alkaline earth metal and zinc, such as calcium, magnesium, barium, and stolon CHUUMU, can be mentioned, and these metal components are used in the form of an oxide, a hydroxide, or a water-soluble salt.
[0064] the [these / periodic table] -- II group metal component -- general -- the form of a silicate -- a particle front face -- or although it exists in the pore of a particle further, even if the part exists in the form of an oxide, a hydroxide, or a carbonate, it does not interfere.
[0065] Various approaches are adopted for processing of the metal component which mentioned the amorphous silica particle above. for example, the aquosity slurry of an amorphous silica spherical particle -- preparing -- the inside of this aquosity slurry -- the [like milk of lime or a magnesium hydroxide / periodic table] -- the water solution thru/or aquosity slurry of a hydroxide of II group metal -- pouring -- this hydroxide -- the front face of an amorphous silica particle -- deposition -- or it is made to react As an aquosity slurry of an amorphous silica particle, it is good to use concentration 5 thru/or 25% of slurry. In a hydroxide, in order to make it react, generally it is good for a particle front face deposition thru/or to perform 1 thru/or stirring processing of 10 hours at 10 thru/or the temperature of 100 degrees C. A reactant is filtered, it rinses as occasion demands and the porosity spherical silicate particle considered as a request is obtained by drying thru/or calcinating. Generally desiccation thru/or baking are 600 degrees C in 80 thru/or temperature, and is good 30 minutes thru/or to carry out for about 30 hours.
[0066] as an exception method -- the [periodic table] -- a porosity spherical silicate particle can also be manufactured by adding to the aquosity slurry of the amorphous silica particle which mentioned above water solutions, such as the water-soluble salts of II group metal, for example, a chloride, a nitrate, and a sulfate, adding hydroxylation alkali and neutralizing as occasion demands.
[0067] the [periodic table] -- there is an inclination which will serve as a detailed lamellar crystal in X diffraction study if it is amorphous in X diffraction study at 10 or less % of the weight and 10 % of the weight is exceeded

although used by the weight ratio which II group metal component is oxide criteria, and was mentioned above. the [moreover, / periodic table] -- fixed relation also between the addition (reacting weight) of II group metal and specific surface area is, it mentions above, and also inside, in a comparatively low amount or a comparatively high amount, specific surface area increases and a weight ratio also has the inclination for specific surface area to fall, with the amount which is whenever [middle].

[0068] According to "ink jet recording paper" this invention, the porosity spherical silicate particle mentioned above is prepared in the front face of bases, such as paper, or is inner-**(ed) to Kaminaka, and let it be a record element for ink jets. It is good per [0.5] whole thru/or to use especially a porosity spherical silicate particle at 3 thru/or 20 % of the weight 40% of the weight.

[0069] for preparing the coat layer of this filler in base front faces, such as paper, -- said filler -- 5 thru/or 40 % of the weight -- especially -- 10 thru/or 25 % of the weight, and the need -- a binder -- 1 thru/or 15 % of the weight -- especially -- 2 thru/or the aquosity slurry included 10% of the weight -- manufacturing -- a filler -- 3 thru/or 20 g/m2 -- especially -- 5 thru/or 15 g/m2 It applies and dries in the amount of coating which becomes.

[0070] as a binder, an aquosity system binder is advantageous, for example, aquosity latex system binders, such as self-emulsification mold binder; styrene-butadiene copolymer latexes, such as water-soluble binder; self-emulsification mold acrylic resin, such as carboxymethylcellulose, ethyl cellulose, a hydroxyethyl cellulose, starch, carboxymethyl starch, cyanoethylation starch, casein, gum arabic, tragacanth gum, a dextrin, polyvinyl alcohol, vinyl ether / maleic-acid copolymer, a polyvinyl pyrrolidone, and water-soluble acrylic resin, etc. are used.

[0071] moreover -- for inner-**(ing) said filler to Kaminaka -- the slurry for paper making -- said filler -- blending -- the inside of paper fiber -- per [1] fiber weight thru/or 20 % of the weight -- especially -- 2 thru/or 10% of the weight of a filler -- ****** rare ** -- what is necessary is just to make it like

[0072] In this invention, it can be independently used as a filler for ink jet record, and also a porosity spherical silicate particle can also be used combining other well-known fillers, for example, a kaolin, the usual silica, a calcium carbonate, etc. in itself.

[0073]

[Example] This invention is explained further, referring to the following example.

[0074] the container made from stainless steel of 1-2300l. of examples -- marketing No. 3 sodium silicate (SiO2 -- 27.8%) Na2 O After adding SiO2/Na2 O=3.19 9% 50.4kg (SiO2 in [all] volume as concentration 7%), and 83.9kg of water, In addition, it adjusts to 30 degrees C after distribution enough 1.2kg (8% of moisture) of powder of a carboxymethyl cellulose (whenever [etherification] 1.34 or 1-% of the weight viscosity 230cp), stirring. Subsequently, 64.5kg of 5% sulfuric acids beforehand adjusted to 30 degrees C is slowly poured into the bottom of stirring, stirring after pouring termination was stopped, it put at the temperature for 12 hours, and the spherical silica particle which is the precursor of this invention was deposited. Next, 33kg of sulfuric acids of 14% of concentration was added to the slurry of the spherical silica particle of this gel, and deNa processing was performed to the bottom of stirring for 1 hour. (pH at this time was 3.4) Next this slurry was filtered and rinsed and the water cake of the precursor silica spherical particle for the formation of porosity compound with a particle size of about 6 micrometers was obtained. (Sample 1-0)

Next, slurry 3kg cracked after dilution so that the solid content of this water cake might change to 10% is put into the beaker made from stainless steel of 5L. The magnesium-hydroxide powder (Kami-shima # made from chemistry 200) which corresponds to 5% (example 1) and 12.5% (example 2) by MgO conversion is added. enough -- after distribution and under a hot bath under churning -- it is -- up to 98 degrees C -- a heating temperature up -- carrying out -- the temperature -- 8 hours -- processing -- after that filtration and rinsing -- carrying out -- 110-degree C constant temperature -- overnight desiccation was carried out with the oven. The sample mill ground the dry letter object of a block, and spherical porosity magnesium-silicate powder was obtained. these powder -- description was shown in Table 1, the scanning electron microscope photograph of the particle of an example 2 was shown in drawing 1 , and the X diffraction Fig. was shown in drawing 2 . Measurement of description was performed by the approach below.

the examining method (1) grain-size Coulter counter (TA[by the coal tar electronics company]- 11) -- it measured using aperture tube 50micrometer by law.

(2) 20 typical particles were chosen from the photograph image obtained with the particle-size scanning electron microscope (made in [S-570] Hitachi) by SEM, the diameter of a particle image was measured using the scale, and the average was shown as a diameter of a primary particle.

(3) 20 typical particles were chosen from the photograph image obtained with the sphericity scanning electron microscope (made in [S-570] Hitachi), the major axis and minor axis of a particle image were measured using the

scale, and the average was calculated from the following formulas (3).
Sphericity = the solvent (alpha-Prome naphthalene, kerosine) of refractive-index known is prepared using the refractive-index meter of a minor axis (Ds) / major-axis (Dl) x100(4) ******** ABBE. Subsequently, according to the oil immersion method of Larsen, several mg sample powder is taken on slide glass, one drop of solvent, in addition the cover glass of refractive-index known are covered, and it observes and asks for migration of a Becke line with an optical microscope.
(5) Specific surface area, Sorptomatic made from pore volume cull ROERUBA Series 1800 was used and it measured with the BET adsorption method.
(6) Chemical composition JIS M-8852 It measured based on the quartzite analysis method, and measured using the atomic absorption method depending on the need.
(7) JIS of an oil absorption pigment test method Oil absorption was calculated based on K5101-21.
(8) JIS of a pH value pigment test method It measured based on K5101-26(3) and (3.1).
(9) N butylamine titrimetric method [bibliography with which the amount measurement of solid acid uses the Hammett indicator : the total amount of solid acid of electric dissociation exponent-3.0-+4.8 was measured by "catalyst" Vol.11, No.6, and p.210-216(1969)].
[0075] It adjusted with water so that the amount of CMC might be set to 0.9kg in the three to example 4 example 1 and total weight might grow into tales doses, and the water cake of a porosity compound-ized precursor silica spherical particle with a particle size of about 12 micrometers was obtained like the example 1 except having made solution temperature into 10 degrees C further. (Sample 2-0) Magnesium-hydroxide compound-ized processing was performed so that it might next become 5% (example 3) and 12.5% (example 4) by MgO conversion like an example 1, and spherical porosity magnesium-silicate powder was obtained. these powder -- description was shown in Table 1.

[0076] The reagent zinc nitrate (Wako Pure Chem Zn (NO3) and 6H2 O) which corresponds to 5% considering 10% silica slurry prepared in the example 1 as the bottom ZnO of 3kg **** picking and churning is added to the beaker of example 55L small quantity every, and it dissolves in it. Next, aqueous ammonia was added small quantity every 28%, it was under hot bath, the heating temperature up was carried out to 98 degrees C after adjusting pH to 9.2-9.5, and it processed at the temperature for 8 hours, and prepared like the example 1 after that, and spherical porosity silicic-acid zinc powder was obtained. these powder -- description was shown in Table 1.
[0077] The reagent calcium chloride (Wako Pure Chem CaCl2 and 2H2 O) which corresponds to 2% considering 10% silica slurry prepared in the example 2 as the bottom CaO of 3kg **** picking and churning is added to the beaker of example 65L small quantity every, and it dissolves in it. Next, aqueous ammonia was added small quantity every 28%, it was under hot bath, the heating temperature up was carried out to 98 degrees C after adjusting pH to 10.0-10.5, and it processed at the temperature for 8 hours, and prepared like the example 1 after that, and spherical porosity calcium silicate powder was obtained. these powder -- description was shown in Table 1.
[0078] It compared as the example 1 of a comparison - a 3 marketing indeterminate form-like silica about Syloid #620 (example 1 of a comparison), Ms. KASHIRU P-78D (example 2 of a comparison), and Carplex #100 (example 3 of a comparison).
[0079] 25g of polyvinyl alcohol (PVA117 by Kuraray Co., Ltd.) 15% water solutions was added to 10g (110-degree-C desiccation criteria) of samples shown in the example table 2 of a trial as a binder, water was added further, churning distribution was fully carried out with 60g of whole quantity, nothing, and an agitator, and coating liquid was prepared. The amount of applications is this coating liquid to basis-weight 45 g/m2 stencil paper (= PPC form use) About 10 g/m2 The coated paper for record applied so that it might become was obtained. This coated paper was air-dried and the Beck smoothness after 24-hour desiccation was measured at 60 more degrees C. The result was shown in Table 2. Furthermore, the hard copy of a test pattern was obtained for the dry paper using the canon color printer BJ500 after calender processing. The following tests were performed using this test piece. The result was collectively shown in Table 2.
(10) It is JIS about the smoothness of the paper obtained in the example of the Beck smoothness trial. It measured based on P-8119.
(11) The concentration before and behind exposure was measured and measured for two months with the Minolta color color difference meter about four hues of the black (IN-0011) of the test paper (hard copy) obtained in the example of a color fastness test trial, a Magenta (IN-0012), and cyanogen (IN-0013) yellow (IN-0014).
(12) The concentration (anhydride conversion) which, in addition, goes 250ml pure water to the beaker of 500ml of tests for viscosity, distributing balance picking and the bottom powder of churning, measures by the Brookfield viscometer, and reaches 100cp was measured, and it considered as the test for viscosity.

(13) yellowing -- L, a, and b value (for an initial coloring value, the coloring value after 1 and an exposure test is 2) were measured in the digital color meter after an exposure test for two months, and the following formulas compared the paper applied in the example of the sex test in quest of deltaE.

deltaE= {(L2-L1) 2+(a2-a1)2(b2-b1) 2} 1/2 [0080]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	比較例1	比較例2	比較例3
pH (-/25℃)	8.4	8.8	8.3	8.9	7.9	9.0	7.5	7.1	10.3
固体酸量(meq/g)	0.25	0.51	0.28	0.46	0.18	0.11	0.04	0.03	0.02
真球度	0.85	0.95	0.94	0.95	0.95	0.94	不定形	不定形	不定形
粒径(SEM)(μm) (コールター)(μm)	5~6 6.7	5~6 6.5	12 12.4	12 12.6	5~6 7.1	5~6 6.2	- 12.1	- 7.9	- 3.5
比表面積(m^2/g)	172	390	170	405	218	399	300	350	100
細孔容積(ml/g)	0.48	0.88	0.50	1.02	0.45	0.98	1.10	1.51	0.28
平均細孔半径( )	56	45	59	50	41	49	73	86	56
吸油量	198	169	180	160	170	200	182	230	236
屈折率 (-)	1.47	1.49	1.48	1.49	1.47	1.46	1.44	1.45	1.44
化学組成 (%)									
lg-loss	6.0	9.2	5.1	9.0	4.6	5.1	4.9	4.4	5.1
SiO_2	89.3	79.4	90.1	79.5	90.6	93.0	95.0	95.6	94.9
MO	4.7 (MgO)	11.4 (MgO)	4.8 (MgO)	11.5 (MgO)	4.8 (ZnO)	1.9 (CaO)	-	-	-

[0081]

[Table 2]

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	比較例1	比較例2	比較例3
塗工液粘度100cp値(%)	29	30	31	33	29	28	25	26	22
ベック平滑度(秒)	72	70	58	56	73	65	38	25	41
初期発色 (ブラック)	1.74	1.70	1.73	1.71	1.76	1.69	1.53	1.62	1.19
(マゼンタ)	1.68	1.70	1.69	1.67	1.69	1.70	1.58	1.67	1.21
(シアン)	1.58	1.51	1.55	1.53	1.56	1.50	1.38	1.51	1.10
(イエロー)	1.54	1.50	1.49	1.51	1.49	1.50	1.31	1.54	1.08
退色度 (ブラック)	1.50	1.49	1.47	1.51	1.49	1.51	1.33	1.32	0.98
(マゼンタ)	1.21	1.28	1.19	1.22	1.24	1.20	0.68	0.65	0.49
(シアン)	1.57	1.51	1.54	1.50	1.53	1.47	1.35	1.45	1.01
(イエロー)	1.39	1.35	1.29	1.36	1.31	1.30	0.90	1.10	0.91
黄変性 (△E)	2.31	2.37	2.31	2.34	2.35	2.36	2.85	3.00	3.10

[0082]
[Effect of the Invention] according to this invention -- the [periodic table] -- by containing II group metal component by the specific quantitative ratio, and using the porosity spherical silicate particle of an amorphous substance thru/or a detailed lamellar crystal in X diffraction study, it excels in the color fastness of an ink image, the xanthochroism-proof of paper, and smooth nature, and, moreover, the filler for ink jet record in which the coating in high concentration is possible can be offered.

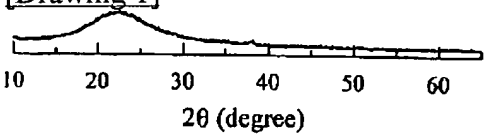
[Translation done.]

* NOTICES *

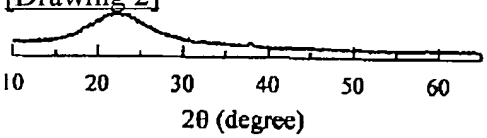
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

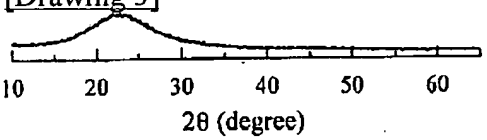
[Drawing 1]



[Drawing 2]

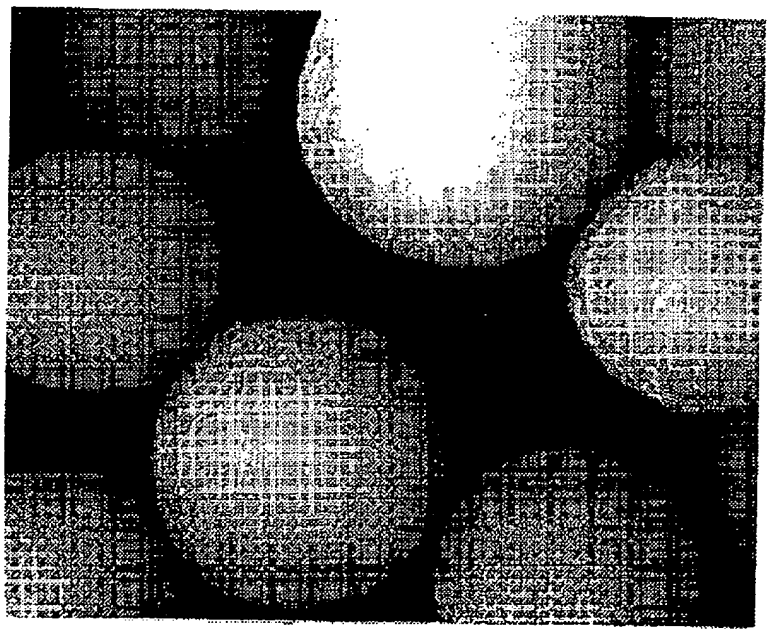


[Drawing 3]



[Drawing 4]

図面代用写真



[Drawing 5]

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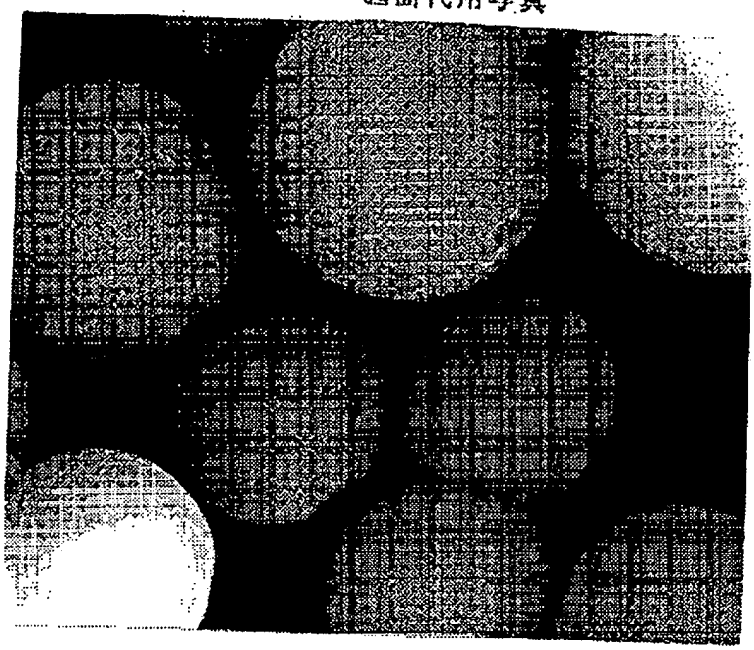
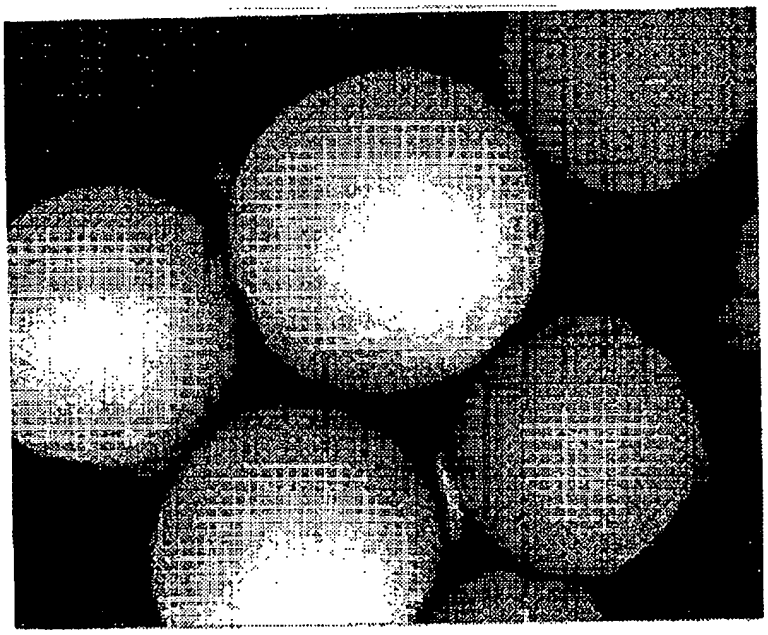


[Drawing 6]

図面代用写真



[Translation done.]